HEXAARYLETHANES CONTAINING THE PHENANTHRENE NUCLEUS

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the University of Michigan

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BY

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PHENANTHRENE DERIVATIVES. VIII. HEXAARYLETHANES CONTAINING THE PHENANTHRENE NUCLEUS*

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Received September 17, 1937

Although attempts have been made to explain the spontaneous reversible dissociation of colorless hexaarylethanes into colored triarylmethyl radicals, no theory has as yet been entirely satisfactory. According to the conception of steric hindrance the aryl groups, in virtue of their size, prevent the aliphatic carbon atoms from approaching each other closely enough to form a normal carbon-carbon bond. Only roughly, however, does the parallelism between extent of dissociation and size of the aryl groups hold. The more recent resonance theory approaches the problem from the opposite point of view. According to this theory dissociation is attributed not to the weakness of the carbon-carbon bond but to the stability of the radicals produced on dissociation. On this assumption, Pauling and Wheland[1] have attempted to show that as the number of possible resonance structures for the radical increases so also does the extent of dissociation of the corresponding hexaarylethane increase. Although a considerable amount of experimental data has been correlated by them, the theory must still be considered qualitative in nature. A combination of steric hindrance and resonance appears to account for the dissociation in a more satisfactory manner.[2]

From the standpoint of both steric hindrance and resonance a study of the dissociation-promoting effect of the phenanthrene nucleus appeared particularly attractive. Indeed, Ingold[3] has recently predicted that the 9-phenanthryl group should possess a greater dissociating power than any group previously investigated. The phenanthrene nucleus provides the additional opportunity of studying the effect on dissociation of isomeric

* From the Ph. D. dissertation of M. C. Kloetzel.

[1] PAULING AND WHELAND, *J. Chem. Phys.*, **1**, 362–374 (1933).

[2] BENT, CUTHBERTSON, DORFMAN, AND LEARY, *J. Am. Chem. Soc.*, **58**, 165–170 (1936); BENT AND CUTHBERTSON, *ibid.*, **58**, 170–173 (1936); BENT AND CLINE, *ibid.*, **58**, 1624–1627 (1936).

[3] INGOLD, *Trans. Faraday Soc.*, **30**, 52–57 (1934). From resonance considerations Ingold has predicted the order of decreasing effect of aryl groups in promotion of radical stability to be; 9-phenanthryl, α-anthryl, α-naphthyl, β-naphthyl, *p*-biphenyl, *m*-biphenyl, phenyl.

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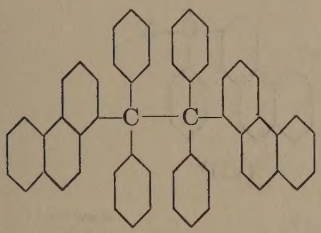
linkage to the aliphatic carbon atom. We have, accordingly, undertaken the synthesis and determination of the extent of dissociation of the following hexaarylethanes: *sym*-di-1-phenanthryltetraphenylethane (I), *sym*-di-2-phenanthryltetraphenylethane (II), *sym*-di-3-phenanthryltetraphenylethane (III), *sym*-di-9-phenanthryltetraphenylethane (IV) and *sym*-di-9-phenanthryldibiphenyleneethane (V).



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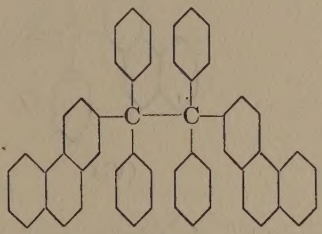

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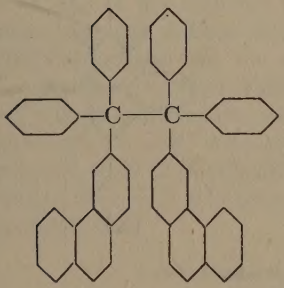

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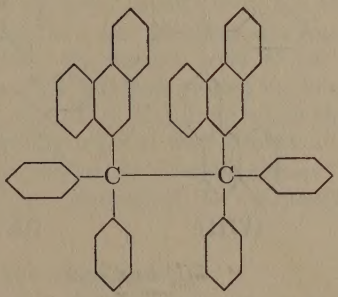

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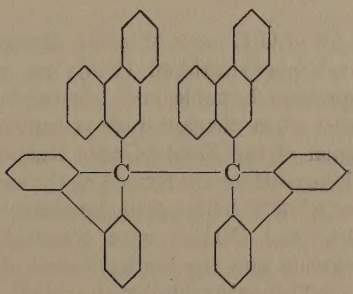

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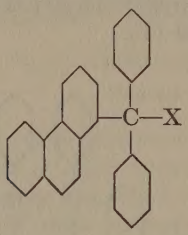
SYNTHESIS OF PHENANTHRYLDIARYLMETHANE DERIVATIVES

In formulas VI-X inclusive are represented the compounds that were prepared either as intermediates or for purposes of characterization.



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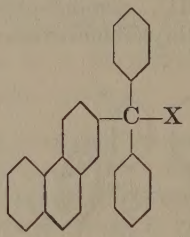

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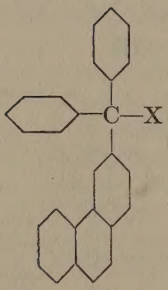

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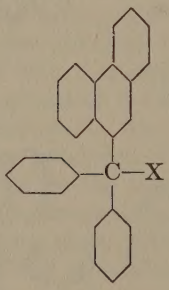

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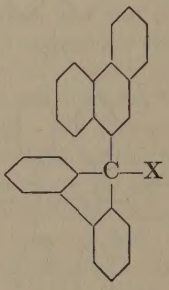


(X)

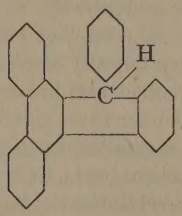
(*a*) X = OH
(*b*) X = Cl
(*c*) X = OCH_3
(*d*) X = OC_2H_5
(*e*) X = Na
(*f*) X = H
(*g*) X = COOH

The triarylcarbinols (X = OH) were obtained through the Grignard reaction. 1-Phenanthryldiphenylcarbinol (VI*a*) was prepared by interaction of phenylmagnesium bromide and 1-benzoylphenanthrene. The latter ketone is formed when phenanthrene is benzoylated according to the Perrier modification of the Friedel-Crafts reaction.[4] We have now found that 9-benzoylphenanthrene is formed at the same time in approximately equal amounts. 2-Phenanthryldiphenylcarbinol (VII*a*) and 3-phenanthryldiphenylcarbinol (VIII*a*) were obtained by interaction of phenylmagnesium bromide and the methyl esters of the corresponding phenanthroic acids. 9-Phenanthryldiphenylcarbinol (IX*a*) and 9-phen-

[4] Bachmann, *J. Am. Chem. Soc.*, **57**, 555-559 (1935).

anthrylbiphenylenecarbinol (X*a*) were most conveniently prepared from 9-phenanthrylmagnesium bromide and benzophenone and fluorenone respectively.

The triarylchloromethanes (X = Cl), with the exception of 9-phenanthryldiphenylchloromethane, were prepared from the carbinols by means of hot acetyl chloride. When heated with acetyl chloride, 9-phenanthryldiphenylcarbinol was converted by loss of a molecule of water into 1,2,3,4-dibenzo-9-phenylfluorene (XI); the triarylchloromethane was obtained



(XI)

by treating the powdered carbinol with cold acetyl chloride. For purposes of characterization the methyl ethers (X = OCH_3) and the ethyl ethers (X = OC_2H_5) of the carbinols were prepared, usually from the triarylchloromethane and sodium alcoholate, in a few instances also from the triarylchloromethane and the alcohol. By reaction with 45 per cent. sodium amalgam the methyl ethers of the carbinols yielded the intensely colored triarylmethylsodium compounds (X = Na), from which the triarylmethanes (X = H) were obtained by reaction with alcohol, and the triarylacetic acids (X = COOH) by reaction with carbon dioxide. The triarylmethanes were also prepared by reduction of the triarylcarbinols by hydriodic acid.

PREPARATION OF THE FREE RADICALS

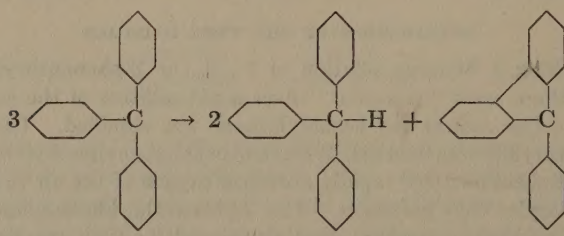
By shaking a benzene solution of 1-, 2-, or 3-phenanthryldiphenylchloromethane with "molecular" silver a red solution of the equilibrium mixture of free radical and hexaarylethane was obtained. The radicals, 1-phenanthryldiphenylmethyl, 2-phenanthryldiphenylmethyl and 3-phenanthryldiphenylmethyl, rapidly absorbed oxygen of the air to give crystalline triarylmethyl peroxides. The 2-phenanthryldiphenylmethyl and 3-phenanthryldiphenylmethyl were also tested for their reaction toward iodine; it was found that in dilute solutions the radicals absorbed 63–69 per cent. of the theoretical amount of iodine necessary to form the triarylmethyl iodide, the reaction being reversible. Solutions of the radicals were found to be relatively stable; they could be kept a week or two without deterioration when protected from light. Of the three hexaaryl-

ethanes only *sym*-di-3-phenanthryltetraphenylethane (III) was isolated in a crystalline form.

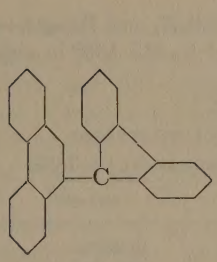
From the standpoint of testing Ingold's prediction in regard to the effectiveness of the 9-phenanthryl group in promoting dissociation, it was unfortunate that 9-phenanthryldiphenylmethyl proved to be an unstable radical. Silver abstracted the halogen quantitatively from 9-phenanthryldiphenylchloromethane (IX*b*) to give a deep-brown-red solution. On standing in the dark, at least half of the hexaarylethane decomposed in thirty minutes, undoubtedly through the radical stage, and after seventy-two hours the solution had lost its color. That all of the triarylchloromethane had been initially converted to the radical was shown by shaking a solution of 9-phenanthryldiphenylchloromethane with silver in the presence of oxygen. Under these conditions the theoretical volume of oxygen was absorbed and crystalline bis(9-phenanthryldiphenylmethyl) peroxide was isolated in excellent yield from the reaction mixture. The reaction between 9-phenanthryldiphenylchloromethane and silver follows the normal course to give the radical 9-phenanthryldiphenylmethyl, which then spontaneously decomposes. The same decomposition was observed to take place when the radical was prepared from 9-phenanthryldiphenylmethylsodium by means of tetramethylethylene bromide according to the following formulation.

$$2\ (C_{14}H_9)(C_6H_5)_2C\text{—Na} + (CH_3)_2BrC\text{—}CBr(CH_3)_2 \rightarrow 2\ (C_{14}H_9)(C_6H_5)_2C + (CH_3)_2C{=}C(CH_3)_2 + 2NaBr.$$

Attempts to determine the structure of the product formed in the decomposition reaction were unsuccessful. One of the characteristic reactions of triarylmethyls is disproportionation. With triphenylmethyl the following reaction takes place:



A similar disproportionation of 9-phenanthryldiphenylmethyl would be expected to yield 9-phenanthryldiphenylmethane (IX$_f$) and either 9-phenanthrylbiphenylenemethyl (XII) or 1,2,3,4-dibenzo-9-phenylfluoryl (XIII). None of these compounds, however, was formed. Moreover,



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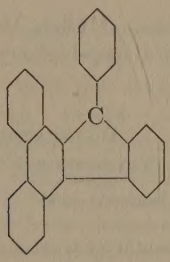

(XIII)

molecular weight determinations made on the product which was isolated to the extent of 96 per cent. showed it to be a dimer of the radical, and it appears likely that 9-phenanthryldiphenylmethyl dimerizes in the same way that triphenylmethyl condenses to give *p*-benzhydryltetraphenylmethane, $2(C_6H_5)_3C \rightarrow (C_6H_5)_2CH—C_6H_4—C(C_6H_5)_3$. Since a number of structures are possible for a dimer of this type from the radical containing the phenanthryl group, no further attempt was made to elucidate the structure. In an attempt to obtain a more stable radical containing the 9-phenanthryl group, *sym*-di-9-phenanthryldibiphenyleneethane (V) was prepared, but the 9-phenanthrylbiphenylenemethyl radical formed from it by dissociation likewise proved to be too unstable to allow a determination of the extent of dissociation of the hexaarylethane.

THE EXTENT OF DISSOCIATION OF THE HEXAARYLETHANES

The extent of dissociation was calculated from the apparent molecular weight of the hexaarylethane as determined by the cryoscopic method. Our first experiments were carried out with the crystalline *sym*-di-3-phenanthryltetraphenylethane (III). The results obtained on different samples of the hexaarylethane were extremely erratic; thus, in nitrobenzene the results indicated 82–134 per cent. dissociation of the hexaarylethane, although the original concentration of the latter was the same in all of the determinations. These results could only be caused by incomplete removal of the solvent from the crystalline hexaarylethane, although the compound was dried at 60° under reduced pressure. Hexaarylethanes are known to form additive compounds with a variety of solvents; among these benzene is noted for the great affinity with which it is held in combination. Addition of acetone to a concentrated benzene solution of hexaphenylethane results in the separation of crystalline hexaphenylethane containing benzene of crystallization,[5] and these are precisely the conditions which obtain in the crystallization of *sym*-di-3-phenanthryl-

[5] GOMBERG, *ibid.*, **24**, 601 (1902).

tetraphenylethane. Müller, Müller-Rodloff, and Bunge[6] found it necessary to heat solid tri-*p*-biphenylmethyl to 155–160° in order to free the

TABLE I

DISSOCIATION OF HEXAARYLETHANES

(Temperature, 5°C.; Concentration, 1.5–3.0%)

HEXAARYLETHANE	SOLVENT	DISSOC., %
sym-Di-1-phenanthryltetraphenylethane	Benzene	32–36
	Nitrobenzene	33–37
sym-Di-2-phenanthryltetraphenylethane	Benzene	16–17
	Nitrobenzene	30–37
sym-Di-3-phenanthryltetraphenylethane	Benzene	11–12
	Nitrobenzene	14
sym-Di-α-naphthyltetraphenylethane	Benzene	28–31[a]
	Nitrobenzene	28–36[b]
sym-Di-β-naphthyltetraphenylethane	Benzene	7–9[c]
sym-Di-*p*-biphenyltetraphenylethane	Benzene	16[d]

[a] Values of 57–62% were obtained by SCHLENK AND RENNING, *Ann.*, **394**, 193 (1912), who isolated the hexaarylethane.

[b] Values of 66–79% were obtained by GOMBERG AND SCHOEPFLE, *J. Am. Chem. Soc.*, **41**, 1655–76 (1919), using the crystalline hexaarylethane.

[c] Values of 27–34% were reported by GOMBERG AND SULLIVAN, *J. Am. Chem. Soc.*, **44**, 1810–33 (1922), who employed the crystalline hexaarylethane.

[d] SCHLENK, WEICKEL, AND HERZENSTEIN, *Ann.*, **394**, 186 (1912), estimated that this hexaarylethane was approximately 15% dissociated at "ordinary temperatures", although they made no determination of its molecular weight. We also made some determinations of the molecular weight of hexa-*p*-biphenylethane by the indirect method. SCHLENK AND WEICKEL, *Ann.*, **372**, 5 (1910), reported that the hexaarylethane was completely dissociated in benzene solutions of 1.43%, 2.28% and 3.33% concentration. In benzene containing 0.93% of the hexaarylethane we found 74% dissociation; in nitrobenzene of 1.05% concentration the degree of dissociation was found to be 65%. The depressions in the freezing points of the solvents with these concentrations are, however, rather small (0.13° and 0.09°). When we attempted to employ concentrations of 2.28%, the concentration of Schlenk and Weickel, some of the hexaarylethane crystallized from the solution in the form of long needles. In the colored solution these crystals appeared to be colorless, but we were unable to obtain them colorless in the dry state.

compound of benzene, and the closely related pentaarylethanes containing the *p*-biphenyl group had to be fused under reduced pressure in order to

[6] MÜLLER, MÜLLER-RODLOFF, AND BUNGE, *Ann* **520**, 251 (1935).

remove solvent of crystallization.[7] Unfortunately, hexaarylethanes are thermally unstable. They should not be heated above 60–70° during the drying process, and this temperature does not always suffice for complete removal of solvent of crystallization. In order to obviate this difficulty we have resorted to the indirect method of determining the apparent molecular weights which does not involve the crystallization of the hexaarylethanes.[8] We have also used the indirect method to determine the extent of dissociation of *sym*-di-α-naphthyltetraphenylethane, *sym*-di-β-naphthyltetraphenylethane and of *sym*-di-*p*-biphenyltetraphenylethane.

A solution containing a weighed amount of phenanthryldiphenylchloromethane in a known weight of solvent was shaken with silver in a nitrogen atmosphere until reaction was complete. A weighed portion of the filtered solution was transferred to the cryoscopic apparatus and the freezing point of the solution was determined. By comparison of this value with the freezing point of the solvent the apparent molecular weight of the hexaarylethane, and from it the extent of dissociation, were calculated. The results of the determinations are shown in Table I.

From the values in Table I it is apparent that the 1- and 2-phenanthryl groups are much more effective than the 3-phenanthryl group in promoting the dissociation of hexaarylethanes. Except for the low values obtained for *sym*-di-2-phenanthryltetraphenylethane in benzene, the substitution of nitrobenzene for benzene had little effect on the degree of dissociation. The 1-phenanthryl,2-phenanthryl and α-naphthyl groups possess a greater dissociating effect than the *p*-biphenyl and 3-phenanthryl groups, and the latter two groups are more effective than the β-naphthyl group. In comparison with other aromatic groups, the 1-phenanthryl, 2-phenanthryl, and α-naphthyl groups can be said to be most effective of all single groups so far investigated in promoting the dissociation of hexaarylethanes.

One of us (M. C. K.) is indebted to the Monsanto Chemical Works for the grant of a fellowship, and to Professor M. Gomberg for his interest and guidance in part of this investigation.

EXPERIMENTAL

1- and 9-Benzoylphenanthrene.—1-Benzoylphenanthrene was prepared from phenanthrene and benzoyl chloride according to the procedure of Bachmann.[4] The by-product gradually crystallized in large prisms. These were purified by recrystallization from ether, and proved to be 9-benzoylphenanthrene; yield, 6%; m.p. 79–81°. Mixed with 9-benzoylphenanthrene prepared from 9-cyanophenanthrene, the melting point was unchanged.

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[7] Bachmann and Wiselogle, *J. Org. Chem.*, **1**, 373 (1936).

[8] Gomberg and Cone, *Ber.*, **37**, 2033–2051 (1904).

1-Phenanthryldiphenylcarbinol (*VI*a).—To a solution of the Grignard reagent prepared from 31.4 g. of bromobenzene in 100 cc. of anhydrous ether was added 28.1 g. of 1-benzoylphenanthrene dissolved in 75 cc. of anhydrous benzene. The mixture was refluxed for six hours, cooled and hydrolyzed with aqueous ammonium chloride. Recrystallization of the residue obtained by evaporation of the benzene-ether layer yielded the carbinol. 1-Phenanthryldiphenylcarbinol crystallizes from benzene-petroleum ether in colorless prisms; m.p. 163–164°; yield, 84%. The carbinol gives a blue-green color with concentrated sulfuric acid.

Anal. Calc'd for $C_{27}H_{20}O$: C, 90.0; H, 5.6.
Found: C, 90.6; H, 5.4.

1-Phenanthryldiphenylchloromethane.—A solution of 15 g. of 1-phenanthryldiphenylcarbinol in 40 cc. of acetyl chloride and 100 cc. of anhydrous benzene was refluxed for eighteen hours. After 50 cc. of solvent was distilled off, 100 cc. of petroleum ether (60–75°) was added. On cooling, 14.6 g. of the carbinol chloride crystallized; an additional quantity, making a total yield of 97%, was obtained by concentration. 1-Phenanthryldiphenylchloromethane crystallizes from benzene in colorless, rectangular prisms; m.p. 212° dec.

Anal. Calc'd for $C_{27}H_{19}Cl$:Cl, 9.4. Found: Cl, 9.2.

Although the chloride forms colored coördination compounds with stannic chloride, ferric chloride and zinc chloride, none of these was obtained in the crystalline form.

Methyl ether of 1-phenanthryldiphenylcarbinol.—To a solution of 4 g. of 1-phenanthryldiphenylchloromethane in 30 cc. of anhydrous benzene was added a solution of 0.8 g. of sodium in 20 cc. of methanol. A precipitate of sodium chloride was immediately produced on mixing. After being refluxed for thirty minutes the mixture was poured into water and the benzene layer was washed, dried and evaporated. The methyl ether crystallizes from acetone-methanol in colorless, hexagonal plates; m.p. 198–199°; yield, 88%.

Anal. Calc'd for $C_{28}H_{22}O$: C, 89.8; H, 5.9.
Found: C, 89.9; H, 5.9.

The *ethyl ether of 1-phenanthryldiphenylcarbinol*, prepared in the same manner as the methyl ether, crystallizes from acetone-ethanol in thin, colorless plates; m.p. 151–152°; yield, 87%.

Anal. Calc'd for $C_{29}H_{24}O$: C, 89.6; H, 6.2.
Found: C, 89.9; H, 6.3.

1-Phenanthryldiphenylmethane.—A mixture of 0.8 g. of the methyl ether of 1-phenanthryldiphenylcarbinol, 30 cc. of anhydrous benzene, 20 cc. of anhydrous ether and 3 g. of 45% sodium amalgam was shaken for eighteen hours in a glass-stoppered cylinder in a nitrogen atmosphere. After freezing the amalgam, 0.5 cc. of ethanol was added to the intense-green solution of 1-phenanthryldiphenylmethylsodium. The resulting decolorized solution was poured into water, the ether solution was dried and the solvent was evaporated. By recrystallization of the residue from benzene-ethanol the 1-phenanthryldiphenylmethane was obtained in 91% yield as colorless prisms; m.p. 175–176°.

Anal. Calc'd for $C_{27}H_{20}$: C, 94.1; H. 5.9.
Found: C, 94.4; H, 5.9.

1-Phenanthryldiphenylacetic acid.—Dry carbon dioxide was passed into a solution of 1-phenanthryldiphenylmethylsodium, prepared from 1.0 g. of the methyl ether, until the color of the organosodium derivative had completely disappeared. The solution was shaken with dilute hydrochloric acid and the benzene solution was separated, concentrated and treated with petroleum ether, whereupon the 1-phenanthryl-

diphenylacetic acid crystallized; yield, 87%. By another recrystallization from benzene-petroleum ether the acid was obtained as clusters of colorless needles; m.p. 230–232° dec.

Anal. Calc'd for $C_{28}H_{20}O_2$: C, 86.6; H, 5.2.
Found: C, 86.7; H, 5.2.

sym-*Di-1-phenanthryltetraphenylethane* (*I*).—A mixture of 3 g. of 1-phenanthryldiphenylchloromethane, 3 g. of "molecular" silver[9] (100 mesh) and 50 cc. of dry benzene was shaken for four days in a glass-stoppered cylinder protected from light. All operations involving the free radical were conducted in an atmosphere of carbon dioxide or nitrogen. The deep-red solution was transferred to a bulb and the benzene was distilled off at 43–48° under reduced pressure. The bulb was of the type previously described by Gomberg,[8] modified by the introduction of a ground-glass joint to facilitate removal of the crystalline hexaarylethane. Another small ground-glass joint, connected to a three-way stopcock through which the benzene was distilled off, was sealed onto the upper part of the bulb.

A solution of the residual red oil in 2 cc. of acetone did not deposit any crystals after standing at 0° for forty-eight hours, and addition of 1 cc. of hexane precipitated the hexaarylethane as a red oil which could not be induced to crystallize.

That the reaction of 1-phenanthryldiphenylchloromethane and silver quickly went to completion, resulting in a stable solution of *sym*-di-1-phenanthryltetraphenylethane, was shown by the following oxygen absorption experiments. A solution of 0.7 g. of the carbinol chloride in 12 cc. of bromobenzene was shaken with 0.7 g. of silver and the oxygen absorption was determined by means of the standard apparatus.[10] After being shaken for one hour, the solution absorbed the calculated volume of oxygen within two minutes. After shaking a sample for ninety-six hours, the solution still absorbed the calculated volume of oxygen.

Bis(1-phenanthryldiphenylmethyl) peroxide was obtained when a benzene solution of *sym*-di-1-phenanthryltetraphenylethane, prepared from 0.96 g. of the carbinol chloride, was filtered from silver and silver chloride and exposed to air. The red solution quickly became pale yellow and deposited colorless crystals of the peroxide. After evaporation of the solvent and removal of colored impurities with ether the peroxide weighed 0.65 g. (72% yield). After recrystallization from carbon disulfide the peroxide melted at 175–176° with decomposition. The peroxide is extremely insoluble in all ordinary solvents.

Anal. Calc'd for $C_{54}H_{38}O_2$: C, 90.2; H, 5.3.
Found: C, 89.9; H, 5.3.

2-Phenanthryldiphenylcarbinol (*VII*a).—To the Grignard reagent prepared from 32 g. of bromobenzene in 100 cc. of anhydrous ether was added a solution of 13.6 g. of methyl 2-phenanthroate[11] in 125 cc. of anhydrous benzene. After being refluxed for eight hours, the mixture, which contained a yellow addition product, was hydrolyzed with aqueous ammonium chloride. On addition of petroleum ether to the concentrated benzene extract, the 2-phenanthryldiphenylcarbinol crystallized. Recrystallization from benzene-petroleum ether gave colorless crystals of the carbinol; m.p. 174–175°; yield, 88%. This carbinol has been previously prepared by another method.[4]

2-Phenanthryldiphenylchloromethane was prepared in the same manner as its 1-isomer by warming for one hour a mixture of 15 g. of 2-phenanthryldiphenylcar-

[9] Gomberg and Cone, *ibid.*, **39**, 3286 (1906).
[10] Gomberg and Schoepfle, *J. Am. Chem. Soc.*, **39**, 1661 (1917).
[11] Mosettig and Van De Kamp, *ibid.*, **52**, 3707 (1930).

binol, 15 cc. of acetyl chloride and 75 cc. of anhydrous benzene. 2-Phenanthryldiphenylchloromethane crystallizes from benzene-petroleum ether in clumps of colorless needles; m.p. 160–161°; yield, 96%.

Anal. Calc'd for $C_{27}H_{19}Cl$: Cl, 9.4.
Found: Cl, 9.1.

Coördination compounds of 2-phenanthryldiphenylchloromethane with metal halides.—When 0.01 g. of 2-phenanthryldiphenylchloromethane was dissolved in 5 cc. of a saturated benzene solution of mercuric chloride and the solution was allowed to stand in the cold for several days, the coördination compound crystallized as brown, iridescent needles. Similarly, the red stannic chloride addition compound was obtained in the crystalline form by adding a drop of 18% benzene solution of stannic chloride to the carbinol chloride in benzene. Intensely colored oils were obtained under similar conditions with ferric chloride and zinc chloride, but these could not be induced to crystallize.

The *methyl ether of 2-phenanthryldiphenylcarbinol* was prepared in 75% yield by exactly the same method as its 1-isomer. It was also prepared by refluxing for two hours a mixture of 1 g. of 2-phenanthryldiphenylcarbinol, 50 cc. of methanol and three drops of concentrated sulfuric acid. On cooling of the solution the methyl ether crystallized in 73% yield. The compound is dimorphic: on recrystallization from acetone-methanol it was obtained as long, colorless needles melting at 105–106°; recrystallized from acetone-petroleum ether (60–75°) it formed truncated octahedra melting at 111–112°.

Anal. Calc'd for $C_{28}H_{22}O$: C, 89.8; H, 5.9.
Found: C, 90.0; H, 6.1.

The *ethyl ether of 2-phenanthryldiphenylcarbinol* was prepared according to the procedure described for its 1-isomer, and crystallizes from petroleum ether in large, colorless prisms; m.p. 116–117° yield, 50%.

Anal. Calc'd for $C_{29}H_{24}O$: C, 89.6; H, 6.2.
Found: C, 89.7; H, 6.0.

2-Phenanthryldiphenylmethane was prepared in two ways. An intensely purple-red solution of 2-phenanthryldiphenylmethylsodium was formed by shaking a mixture of 0.75 g. of the methyl ether of 2-phenanthryldiphenylcarbinol and 2.5 g. of 45% sodium amalgam in 25 cc. of anhydrous ether and 25 cc. of anhydrous benzene. After twenty-four hours the amalgam was frozen and enough ethanol was added to decolorize the solution. 2-Phenanthryldiphenylmethane crystallizes from benzene-ethanol in long, colorless needles; m.p. 151–152°; yield, 91%.

The same hydrocarbon was obtained when 2-phenanthryldiphenylcarbinol was reduced with hydriodic acid. A solution of 1 g. of the carbinol in 20 cc. of acetic acid was refluxed for thirty minutes with 2 cc. of hydriodic acid (sp. g. 1.7). Sulfur dioxide was passed into the hot solution in order to remove the iodine which was liberated in the reaction. On being cooled, the solution deposited the 2-phenanthryldiphenylmethane; yield, 77%.

Anal. Calc'd for $C_{27}H_{20}$: C, 94.1; H, 5.9.
Found: C, 94.4; H, 5.9.

2-Phenanthryldiphenylacetic acid was prepared from 2-phenanthryldiphenylmethylsodium in the same manner as described for the 1-isomer. The acid crystallizes from acetic acid in colorless, columnar prisms containing solvent of crystallization; m.p. 232–233°; yield, 82%.

Anal. Calc'd for $C_{28}H_{20}O_2$: C, 86.6; H, 5.2.
Found: C, 86.8; H, 5.1.

sym-*Di-2-phenanthryltetraphenylethane* (*II*).—A cherry-red solution of the radical was obtained by shaking for four days a mixture of 3 g. of 2-phenanthryldiphenylchloromethane and 3 g. of "molecular" silver in 50 cc. of benzene. Oxygen absorption experiments indicated that reaction was complete after this period of time. When three times the amount of silver was used, two hours sufficed for complete reaction. Evaporation of the filtered solution as described for the 1-isomer left a red oil. All attempts to induce crystallization of the oil from acetone, benzene, ethyl acetate, or chloroform resulted in failure. Addition of hexane or methanol, in which the hexaarylethane is extremely insoluble, to solutions of the oil in any of the above solvents always caused deposition of a red oil. When the residual red oil was dissolved in 2 cc. of ether, gummy and poorly-defined crystals were obtained on standing at 0° for twelve hours. All of the solvent could not be removed from the crystals by heating to 60° under reduced pressure, and heating to 100° caused decomposition.

A solution of the radical prepared from 2.0 g. of the carbinol chloride in 50 cc. of benzene absorbed 21.0 cc. (62.7%) of a solution of iodine in benzene (0.02 g. per cc.).

Bis(2-phenanthryldiphenylmethyl) peroxide[4] was obtained in 79% yield by oxidation of the radical with air. A solution of the radical allowed to stand in the dark for six months gave only a 40% yield of the peroxide, an indication that approximately 50% of the radical had undergone decomposition in this period of time.

3-Phenanthryldiphenylcarbinol (*VIII*a).—To the Grignard reagent prepared from 53 g. of bromobenzene in 160 cc. of anhydrous ether was added a solution of 25 g. of methyl 3-phenanthroate[11] in 145 cc. of anhydrous benzene. After being refluxed for eight hours, the mixture was hydrolyzed with aqueous ammonium chloride. From acetone-petroleum ether the carbinol crystallizes in colorless, columnar needles containing solvent of crystallization; m.p. 92–93°; yield, 82%. When the carbinol is crystallized from petroleum ether alone the melting point is raised to 100–102°.

Anal. Calc'd for $C_{27}H_{20}O$: C, 90.0; H, 5.6.
Found: C, 90.3; H, 5.6.

This carbinol produces an intensely purple-blue color with concentrated sulfuric acid. The compound previously described[4] as 3-phenanthryldiphenylcarbinol was in reality the methyl ether of this carbinol, which was probably produced when the carbinol was crystallized in the presence of methanol.

3-Phenanthryldiphenylchloromethane, prepared in the same manner as described for the 2-isomer, crystallizes from benzene-petroleum ether in colorless, rectangular prisms; m.p. 132.5–133.5°; yield, 88%.

Anal. Calc'd for $C_{27}H_{19}Cl$: Cl, 9.4. Found: Cl, 9.3.

A sample of this 3-phenanthryldiphenylchloromethane gave on hydrolysis the carbinol melting at 92–93° after recrystallization from acetone-petroleum ether.

Treated with stannic chloride as described for the 2-isomer, 3-phenanthryldiphenylchloromethane produced a coördination compound in the form of small, deep-red plates having a purple iridescence. The ferric chloride compound was obtained as broad, red, iridescent needles by adding a saturated ethyl acetate solution of ferric chloride to the carbinol chloride in benzene, and the zinc chloride compound separated as small, brown crystals when a 6% ether solution of zinc chloride was added to the carbinol chloride in benzene.

The *methyl ether of 3-phenanthryldiphenylcarbinol*, prepared in 88% yield by the Williamson method as described for the 1-isomer, crystallizes from acetone-methanol in colorless, glistening plates; m.p. 147–148°. The same ether was prepared by refluxing for two hours a solution of 3 g. of 3-phenanthryldiphenylcarbinol in 125 cc.

of methanol containing nine drops of concentrated sulfuric acid. On cooling, the ether crystallized in 87% yield.

Anal. Calc'd for $C_{28}H_{22}O$: C, 89.8; H, 5.9.
Found: C, 90.1; H, 5.8.

The *ethyl ether of 3-phenanthryldiphenylcarbinol* was prepared by refluxing for two hours a solution of 1.8 g. of 3-phenanthryldiphenylcarbinol in 80 cc. of ethanol containing six drops of concentrated sulfuric acid. On cooling and concentrating the solution, a 90% yield of the ether was obtained. The ethyl ether crystallizes from acetone-ethanol in colorless needles; m.p. 155–156°.

Anal. Calc'd for $C_{29}H_{24}O$: C, 89.6; H, 6.2.
Found: C, 89.9; H, 6.3.

3-*Phenanthryldiphenylmethane* was prepared from the intensely purple-red 3-phenanthryldiphenylmethylsodium in the same manner as described for the 2-isomer. The hydrocarbon crystallizes from benzene-ethanol in long, flat, colorless needles; m.p. 122–123°; yield, 83%. 3-Phenanthryldiphenylmethane was also prepared by reduction of 3-phenanthryldiphenylcarbinol by hydriodic acid in the manner described for the 2-isomer.

Anal. Calc'd for $C_{27}H_{20}$: C, 94.1; H, 5.9.
Found: C, 94.3; H, 6.2.

3-Phenanthryldiphenylacetic acid was prepared by the method described for the 1-isomer. Crystallization of the acid from acetic acid produced clusters of colorless needles containing solvent of crystallization which was tenaciously held; yield, 63%. From benzene-petroleum ether the acid was obtained also as needles; m.p. 215–216°.

Anal. Calc'd for $C_{28}H_{20}O_2$: C, 86.6; H, 5.2.
Found: C. 87.0; H, 5.3.

sym-*Di-3-phenanthryltetraphenylethane* (*III*).—A deep-red benzene solution of the radical-ethane equilibrium mixture was prepared from 3 g. of 3-phenanthryldiphenylchloromethane as described for the 1-isomer. The viscous red oil remaining after removal of the benzene under reduced pressure was dissolved in 2 cc. of warm acetone and the hexaarylethane was allowed to crystallize at 0° for twelve hours. The crystalline material was washed several times with cold acetone and finally dried under reduced pressure in a stream of carbon dioxide; m.p. 150–152° dec. (in nitrogen); yield, 2.28 g. (85%). Although the crystalline material was practically colorless when freshly prepared, it rapidly became yellow when exposed to air.

The crystalline hexaarylethane, when dissolved in bromobenzene, absorbed the calculated volume of oxygen at room temperature within two minutes.

A solution of the hexaarylethane prepared from 1.0 g. of the carbinol chloride in 50 cc. of benzene decolorized 11.5 cc. of a benzene solution of iodine (0.02 g. per cc.). This corresponds to 68.6% absorption. When excess iodine was added, the solution became green and a dark oil, presumably a periodide[5] of 3-phenanthryldiphenyliodomethane, was deposited, which crystallized on standing.

Bis(*3-phenanthryldiphenylmethyl*) *peroxide*[4] was obtained in 85% yield by oxidation of a benzene solution of the hexaarylethane with air. A solution of the hexaarylethane which was allowed to stand in the dark for six months gave only a 69% yield of peroxide, an indication that approximately 19% of the hexaarylethane had undergone decomposition during this period of time. The peroxide was best recrystallized from amyl acetate; m.p. 197°.

9-Phenanthryldiphenylchloromethane (*IX*b).—When an attempt was made to prepare this chloride by heating the carbinol[12] with acetyl chloride, there was obtained

[12] Bachmann, *ibid.*, **56**, 1363–1367 (1934).

a good yield of 1,2,3,4-dibenzo-9-phenylfluorene. When the carbinol was treated with dry hydrogen chloride in ether there was also apparently some fluorenation, as the resulting product (m.p. 162–170°) did not contain the calculated amount of chlorine.

9-Phenanthryldiphenylchloromethane was finally successfully prepared by the following method. To 30 g. of the finely powdered 9-phenanthryldiphenylcarbinol was added 75 cc. of acetyl chloride. A reaction soon began and the mixture became warm. It was stirred for a few minutes and then allowed to stand at 0° for two hours. The chloride was filtered off, shaken with petroleum ether for two hours, and again filtered. When all traces of acetyl chloride had been removed in this manner the carbinol chloride could be recrystallized without decomposition from benzene-petroleum ether, and was obtained as colorless, columnar needles; m.p. 182–183° dec.; yield, 80%.

Anal. Calc'd for $C_{27}H_{19}Cl$: Cl, 9.4. Found: Cl, 9.0.

Coördination compounds of this halide could not be prepared, as in every instance fluorenation took place when a solution of the carbinol chloride was allowed to stand in contact with stannic chloride, ferric chloride or zinc chloride.

The *methyl ether of 9-phenanthryldiphenylcarbinol* was prepared in the usual manner from sodium methylate and 9-phenanthryldiphenylchloromethane; yield, 90%. The ether crystallizes from acetone-methanol in colorless, glistening prisms; m.p. 165°.

Anal. Calc'd for $C_{28}H_{22}O$: C, 89.8; H, 5.9.
Found: C, 89.8; H, 5.8.

The *ethyl ether of 9-phenanthryldiphenylcarbinol* was obtained from sodium ethylate and the carbinol chloride. Recrystallization from acetone-petroleum ether gave thin, colorless plates; m.p. 139–140°; yield, 42%.

Anal. Calc'd for $C_{29}H_{24}O$: C, 89.6; H, 6.2.
Found: C, 89.4; H, 6.1.

9-Phenanthryldiphenylmethane was prepared from the intensely green 9-phenanthryldiphenylmethylsodium in the same manner as described for the 2-isomer. The hydrocarbon crystallizes from benzene-ethanol in colorless needles; m.p. 174–175°; yield, 88%. 9-Phenanthryldiphenylmethane has been recently prepared from 9-bromophenanthrene and diphenylbromomethane.[12]

9-Phenanthryldiphenylacetic acid was prepared in the same manner as described for the preparation of the 1-isomer. Crystallization from acetic acid produced long, colorless needles which lost solvent of crystallization at approximately 130° and then melted at 257–259° dec.; yield, 96%.

Anal. Calc'd for $C_{28}H_{20}O_2$: C, 86.6; H, 5.2.
Found: C, 86.2; H, 5.0.

sym-*Di-9-phenanthryltetraphenylethane* (*IV*).—When a mixture of 0.8583 g. of 9-phenanthryldiphenylchloromethane, 1.0 g. of "molecular" silver (100 mesh) and 30 cc. of anhydrous benzene was shaken in a nitrogen atmosphere the solution became brown-red, but the intensity of the color soon began to decrease, and at the end of three days the solution was practically colorless and would absorb no oxygen. Estimation of the silver chloride indicated that the abstraction of the halogen from the carbinol halide had proceeded to the extent of 95–99%.

In each of the following experiments approximately 1 g. of the carbinol chloride in 12 cc. of bromobenzene was shaken with 1 g. of "molecular" silver (100 mesh) for the stated period of time. The oxygen absorption at the ends of these periods was: two minutes, 28%; five minutes, 30%; ten minutes, 26%; thirty minutes, 14%; three hours, 7%; three days, 0%.

When a bromobenzene solution (20 cc.) of the carbinol chloride (1.2 g.) was shaken with silver (5 g., 100 mesh) in the presence of oxygen, quantitative absorption of the latter was obtained within six minutes. From the reaction mixture was isolated a 78% yield of bis(9-phenanthryldiphenylmethyl) peroxide.

9-Phenanthryldiphenylmethyl was also prepared by a method involving the procedure of Ziegler and Schnell.[13] A mixture of 0.8 g. of the methyl ether of 9-phenanthryldiphenylcarbinol, 55 cc. of anhydrous ether and 3 g. of 45% sodium amalgam was shaken in an atmosphere of nitrogen for twenty-four hours. The solution was filtered into a nitrogen-filled bulb and a solution of 0.26 g. of tetramethylethylene bromide in 10 cc. of anhydrous ether was added. The green color of the sodium addition compound immediately gave way to the brown-red of the 9-phenanthryldiphenylmethyl radical. The color soon faded, however, and after standing in the dark for four hours the solution was practically colorless.

Bis(9-phenanthryldiphenylmethyl) peroxide.—The reaction mixture from the production of 9-phenanthryldiphenylmethyl in the presence of oxygen (as previously described) was filtered and the residue was washed with petroleum ether and dried. It was then treated with 3% nitric acid and finally with 28% ammonium hydroxide to remove silver and silver chloride. The remaining material was found to be nearly pure bis(9-phenanthryldiphenylmethyl) peroxide; m.p. 178–179° dec.; yield, 78%. This peroxide was found to be extremely insoluble in most solvents, and relatively unstable to heat, making its recrystallization difficult. A small amount was, however, recrystallized from chloroform-ethanol; m.p. 184–186° dec.

The identity of the peroxide was confirmed by synthesis from sodium peroxide and 9-phenanthryldiphenylchloromethane according to the method of Gomberg.[14] Air, freed from carbon dioxide, was passed through a mixture of 3 g. of 9-phenanthryldiphenylchloromethane, 10 g. of sodium peroxide, 90 cc. of ice water and 40 cc. of benzene until all the benzene was evaporated. The solid residue was boiled with 50 cc. of ether to dissolve the carbinol, and the small insoluble residue was extracted with 125 cc. of carbon disulfide for six hours. Approximately 100 cc. of the solvent was distilled off, and from the remaining solvent 0.05 g. of the colorless, crystalline peroxide separated; m.p. 184–186°; yield, 1.8%.

Anal. Calc'd for $C_{54}H_{38}O_2$: C, 90.2; H, 5.3.
Found: C, 90.1; H, 5.3.

The decomposition product of 9-phenanthryldiphenylmethyl.—Colorless solutions resulting from decomposition of the radical, prepared either from 9-phenanthryldiphenylchloromethane and silver or from 9-phenanthryldiphenylmethylsodium and tetramethylethylene dibromide, yielded the same decomposition products.

A solution of 5 g. of 9-phenanthryldiphenylchloromethane in 65 cc. of anhydrous benzene was shaken in a nitrogen atmosphere with 5 g. of "molecular" silver. After two days the colorless solution contained a colorless precipitate which was filtered off, freed from silver and silver chloride, washed with benzene and dried (3.34 g.). The filtrate on evaporation yielded 0.96 g. of the same product, making the total yield 95% (calculated on the basis of complete removal of chlorine from the carbinol chloride). By fractional crystallization from petroleum ether (60–75°), this product was separated into two fractions: the first crystallized from benzene-petroleum ether in irregular hexagonal plates, and constituted 96% of the total decomposition product. After four recrystallizations the product melted at 222–228° (dec.) in air, and at 275–280° (dec.) in nitrogen. Molecular-weight determination (Menzies

[13] Ziegler and Schnell, *Ann.*, **437**, 244 (1924).
[14] Gomberg, *Ber.*, **33**, 3155 (1900).

boiling-point method in benzene) gave an average value of 646 (theoretical molecular weight of a dimer, 686). The second fraction (4%) crystallized from benzene-ethanol in colorless needles; m.p. 181° (dec.) with previous softening. An average molecular weight of 471 was obtained by the microebullioscopic method of Sucharda and Bobranski.[15]

9-Phenanthrylbiphenylenecarbinol (*X*a) was prepared in 70% yield according to the method of Bachmann.[12] In one instance, a sample crystallized from benzene-petroleum ether melted at 175–176°, solidified, and remelted at 191–192°, the melting point previously reported.

9-Phenanthrylbiphenylenemethyl acetate was obtained as colorless plates when five drops of concentrated sulfuric acid were added to a hot solution of 0.5 g. of 9-phenanthrylbiphenylenecarbinol in 10 cc. of acetic acid, and the vessel was scratched with a glass rod; m.p. 113–115°; yield, 66%.

Anal. Calc'd for $C_{29}H_{20}O_2$: CH_3COO, 14.6. Found: CH_3COO, 14.4.

9-Phenanthrylbiphenylenechloromethane.—A solution of 14.36 g. of 9-phenanthrylbiphenylenecarbinol in 30 cc. of anhydrous benzene was refluxed for three hours with 21 cc. of acetyl chloride. An equal volume of petroleum ether was added and on cooling the solution an 87% yield of the chloromethane crystallized in hexagonal prisms; m.p. 211–212° after recrystallization from benzene-petroleum ether.

Anal. Calc'd for $C_{27}H_{17}Cl$: Cl, 9.4. Found: Cl, 9.4.

Crystalline coördination compounds of 9-phenanthrylbiphenylenechloromethane with stannic chloride and with mercuric chloride were obtained. By repeatedly filtering off the brown, gelatinous precipitate formed when 0.8 g. of the carbinol chloride was dissolved in 20 cc. of a saturated benzene solution of mercuric chloride, a yield of 0.14 g. of the coördination compound was obtained; m.p. 237–240°.

Anal. Calc'd for $C_{14}H_9(C_6H_4)_2C\text{-}Cl \ldots 3HgCl_2$: Cl, 20.8. Found: Cl, 20.9.

Crystallization of the purple-iridescent coördination compound began almost immediately when a solution of 2 g. of stannic chloride in 2 cc. of anhydrous ethylene chloride was added to a solution of 1 g. of 9-phenanthrylbiphenylenechloromethane in 15 cc. of ethylene chloride; m.p. 230° dec.

Anal. Calc'd for $C_{14}H_9(C_6H_4)_2C\text{-}Cl \ldots SnCl_4$: Cl, 27.8. Found: Cl, 27.8.

9-Phenanthrylbiphenylenebromomethane.—After refluxing for one hour a mixture of 14.36 g. of 9-phenanthrylbiphenylenecarbinol, 34.5 g. of acetyl bromide and 30 cc. of anhydrous benzene, an equal volume of petroleum ether was added. The bromomethane crystallized on cooling of the solution; m.p. 230° dec.; yield, 78%.

Anal. Calc'd for $C_{27}H_{17}Br$: Br, 19.0. Found: Br, 18.9.

The *methyl ether of 9-phenanthrylbiphenylenecarbinol* was prepared from 9-phenanthrylbiphenylenechloromethane in the same manner as described for the preparation of the methyl ether of 1-phenanthryldiphenylcarbinol. Crystallization from acetone gave colorless, diamond-shaped plates; m.p. 231–232°; yield, 74%.

Anal. Calc'd for $C_{28}H_{20}O$: C, 90.3; H, 5.4.
Found: C, 90.3; H, 5.4.

The *ethyl ether of 9-phenanthrylbiphenylenecarbinol* was prepared in the usual manner from 2.25 g. of 9-phenanthrylbiphenylenebromomethane and sodium ethylate. The ether crystallizes from acetone-ethanol in colorless, diamond-shaped plates; m.p. 161–162°, solidifying, and remelting at 173–174°; yield, 40%.

Anal. Calc'd for $C_{29}H_{22}O$: C, 90.1; H, 5.7.
Found: C, 90.1; H, 5.6.

9-Phenanthrylbiphenylenemethane was prepared by refluxing for four hours a mix-

[15] Sucharda and Bobranski, *Chem. Abstr.*, **23**, 2853 (1929).

ture of 1.79 g. of 9-phenanthrylbiphenylenecarbinol, 100 cc. of ethanol and 16 g. of zinc dust, during which time a total of 45 cc. of 36% hydrochloric acid was added in small portions. Some of the hydrocarbon separated during the addition of the hydrochloric acid. The mixture was filtered, and the filtrate was concentrated and cooled, whereupon the hydrocarbon crystallized. Extraction of the residue on the filter with benzene yielded more hydrocarbon. 9-Phenanthrylbiphenylenemethane crystallizes from benzene in colorless, diamond-shaped plates; m.p. 192–193°; yield, 90%. The hydrocarbon prepared in this manner was identical with that obtained from 9-bromofluorene and 9-phenanthrylmagnesium bromide.[12]

sym-*Di-9-phenanthryldibiphenyleneethane* (*V*).—On shaking the chloride in bromobenzene with silver, a brown-red solution of 9-phenanthrylbiphenylenemethyl was obtained. The following oxygen absorptions were obtained with such solutions shaken for varying periods of time: after one hour, 82%; after twenty hours, 20%; after seventy-two hours, 9%. When the carbinol bromide was shaken with silver and bromobenzene in the presence of oxygen, quantitative absorption of the latter was obtained within twenty minutes.

Bis(9-phenanthrylbiphenylenemethyl) peroxide was obtained when a brown-red solution of 9-phenanthrylbiphenylenemethyl, prepared by shaking a mixture of 1.42 g. of 9-phenanthrylbiphenylenebromomethane, 3 g. of "molecular" silver (80 mesh) and 40 cc. of anhydrous benzene for thirty-five minutes, was exposed to air. The solution became red and deposited 0.75 g. (62.5%) of the colorless, crystalline peroxide. After recrystallization from toluene the peroxide melted at 208–210° dec.

Anal. Calc'd for $C_{54}H_{34}O_2$: C, 90.7; H, 4.8.
Found: C, 90.6; H, 4.7.

1,2,3,4-Dibenzo-9-phenylfluoryl acetate.—Seven g. of lead dioxide was added to the boiling solution of 7 g. of 1,2,3,4-dibenzo-9-phenylfluorene[12] in 210 cc. of acetic acid over a period of one-half hour. After all the lead dioxide had been added the solution was refluxed for one hour more, enough water was added to the hot solution to start crystallization, and the solution was cooled. Recrystallization from acetone removed most of the colored impurities from the precipitated acetate. After sublimation *in vacuo* (250°/0.4 mm.) and recrystallization from acetic acid, the acetate melted at 254–255°; yield, 66.5%.

Anal. Calc'd for $C_{29}H_{20}O_2$: C, 87.0; H, 5.0.
Found: C, 86.9; H, 4.9.

A 0.5 g. sample of the acetate was reduced by heating for one hour with 0.5 g. of red phosphorus, 0.5 g. of iodine, 1 cc. of water and 15 cc. of acetic acid. The hot filtered solution was poured into water and the precipitated product was recrystallized from acetic acid; yield of 1,2,3,4-dibenzo-9-phenylfluorene, 90%; m.p. 210–212°.

1,2,3,4-Dibenzo-9-phenylfluorenol was obtained when an alcoholic solution of the acetate was heated for several minutes with potassium hydroxide and the solution was acidified with hydrochloric acid. The mixture was diluted with water and the carbinol extracted with benzene. The residue remaining when the solution was evaporated was sublimed *in vacuo* (250–260°/0.4 mm.) and the carbinol was obtained as square, colorless tablets on recrystallization from benzene-petroleum ether; m.p. 181°. The carbinol gives a deep-red color with concentrated sulfuric acid.

Anal. Calc'd for $C_{27}H_{18}O$: C, 90.5; H, 5.1.
Found: C, 90.8; H, 5.1.

1,2,3,4-Dibenzo-9-phenyl-9-chlorofluorene.—A mixture of 1.79 g. of 1,2,3,4-dibenzo-9-phenylfluoryl acetate, 3 cc. of acetyl chloride and 20 cc. of anhydrous benzene was refluxed for three hours, and an equal volume of petroleum ether (90–

TABLE II

MOLECULAR-WEIGHT DETERMINATIONS OF THE HEXAARYLETHANES

(Molecular Depression Constants: Nitrobenzene, 69.7; Benzene, 51.7)

WEIGHT SOLVENT (g.)	WEIGHT SOLUTE (g.)	CONC. (%)	F.P. DEPRESSION (degrees)	DISSOC. (%)
sym-Di-1-phenanthryltetraphenylethane in Benzene				
16.19	0.2791	1.69	0.176	36
17.43	0.2629	1.49	0.150	32
sym-Di-1-phenanthryltetraphenylethane in Nitrobenzene				
23.89	0.5319	2.18	0.310	37
20.66	0.4792	2.26	0.315	34
23.44	0.6043	2.51	0.347	33
sym-Di-2-phenanthryltetraphenylethane in Benzene				
19.80	0.3539	1.76	0.157	17
16.25	0.2790	1.69	0.150	16
sym-Di-2-phenanthryltetraphenylethane in Nitrobenzene				
19.77	0.4545	2.24	0.320	37
21.34	0.4476	2.05	0.284	33
23.32	0.5347	2.24	0.303	30
27.06	0.4951	1.80	0.241	30
sym-Di-3-phenanthryltetraphenylethane in Benzene				
15.78	0.4446	2.74	0.237	12
17.57	0.3181	1.78	0.151	11
17.51	0.5280	2.93	0.251	11
sym-Di-3-phenanthryltetraphenylethane in Nitrobenzene				
19.64	0.4625	2.30	0.273	14
23.02	0.6006	2.54	0.301	14
24.04	0.7837	3.16	0.377	14[a]
sym-Di-α-naphthyltetraphenylethane in Benzene				
18.99	0.4670	2.40	0.285	31
15.47	0.3419	2.16	0.250	28
sym-Di-α-naphthyltetraphenylethane in Nitrobenzene				
24.80	0.5446	2.14	0.356	36
18.23	0.4558	2.44	0.385	28
sym-Di-β-naphthyltetraphenylethane in Benzene				
17.54	0.4282	2.38	0.235	9
15.46	0.3773	2.38	0.231	7

[a] This determination was made employing the original indirect method of Gomberg and Cone[3], wherein the hexaarylethane solution was prepared directly in the freezing vessel by stirring the chloride with three times its weight of 100 mesh silver for three hours.

TABLE II—*Concluded*

WEIGHT SOLVENT (g.)	WEIGHT SOLUTE (g.)	CONC. (%)	F.P. DEPRESSION (degrees)	DISSOC. (%)
sym-Di-*p*-biphenyltetraphenylethane in Benzene				
17.00	0.4104	2.36	0.226	16
18.17	0.5771	3.08	0.298	16
Hexa-*p*-biphenylethane in Benzene				
18.44	0.1738	0.93	0.090	74
Hexa-*p*-biphenylethane in Nitrobenzene				
20.32	0.2160	1.05	0.130	65

100°) was added. Fifteen cc. of benzene was then distilled off, the solution was cooled to 0°, and crystallization was induced by scratching with a glass rod. Recrystallization from benzene-petroleum ether gave a 50% yield of the carbinol chloride; m.p. 172–174°.

Anal. Calc'd for $C_{27}H_{17}Cl$: Cl, 9.4. Found: Cl, 9.5.

A solution of 0.10 g. of 1,2,3,4-dibenzo-9-phenyl-9-chlorofluorene in 10 cc. of anhydrous benzene was shaken in a sealed tube with 0.2 g. of 100-mesh "molecular" silver. The red color of 1,2,3,4-dibenzo-9-phenylfluoryl quickly appeared, and the solution retained its color even after twelve hours. The red solution on exposure to air was quickly decolorized, and the colorless peroxide was deposited; m.p. 209–211° dec. The peroxide gives a red color with concentrated sulfuric acid.

Molecular-weight determinations of the hexaarylethanes.—Gomberg and Cone[8] were the first to determine the molecular weight of a hexaarylethane without previously isolating it. Subsequently the indirect method was used in a number of instances to determine the extent of dissociation of hexaarylethanes.[16]

We employed the Beckmann cryoscopic method for the molecular-weight determinations, modified for the use of an atmosphere of nitrogen.[17] One side-arm of the freezing vessel was fitted with a rubber stopper through which passed a stopcock which was used for evacuating the apparatus, and the second side arm was fitted with a rubber stopper through which passed a glass siphon of the same type as that used in connection with the bulb. A solution containing a carefully weighed sample of the halide in a known weight of solvent was shaken for twelve hours in a glass-stoppered cylinder in a nitrogen atmosphere, the cylinder being wrapped in a black cloth to prevent entrance of light. By means of oxygen absorption experiments on separate samples it was shown that in every instance the reaction had gone to completion and that there had been no decomposition of the radical during this period of time. The silver was allowed to settle, the stopper was removed from the cylinder, and the siphon connected to the cryoscopic apparatus was quickly inserted in its place. An aliquot portion of the radical solution was then transferred to the nitrogen-filled cryoscopic apparatus, the weight so transferred being determined by weighing the freezing vessel at the end of the run. Determination of the freezing point of this

[16] Gomberg and Forrester, *J. Am. Chem. Soc.*, **47**, 2373–2391 (1925); Gomberg and McGill, *ibid.*, **47**, 2400 (1925); Lund, *ibid.*, **49**, 1349 (1927).

[17] Beckmann, *Z. physik. Chem.*, **44**, 170 (1903).

solution, together with a similar determination on a sample of pure solvent from which the solution had been made, then gave the requisite data for calculation of the molecular weight. From the molecular weight was calculated the dissociation of the hexaarylethane.

$$\text{Dissociation} = \frac{\text{M.W.}_c}{\text{M.W.}_f} - 1,$$

where M.W._c is the calculated molecular weight of the hexaarylethane and M.W._f is the molecular weight found.

Upon completion of each determination the radical solution was oxidized and, after evaporation of the solvent, the total oxidation products were weighed as peroxide. The weight of peroxide in every instance checked the theoretical weight to within 90%.

The results of the molecular weight determinations are shown in Table II.

SUMMARY

(1) *sym*-Di-1-phenanthryltetraphenylethane, *sym*-di-2-phenanthryltetraphenylethane and *sym*-di-3-phenanthryltetraphenylethane have been synthesized, the latter being obtained in the crystalline state.

(2) The dissociation of these hexaarylethanes has been determined in benzene and in nitrobenzene. The 1- and 2-phenanthryl groups have been found to rank with the α-naphthyl group in being more effective in promoting dissociation than any other aromatic group thus far investigated. The 3-phenanthryl group was found to be less than half as effective.

(3) 9-Phenanthryldiphenylmethyl and 9-phenanthrylbiphenylenemethyl were prepared, but were found to be too unstable to allow molecular weight determinations of the corresponding hexaarylethanes.

(4) A number of new phenanthryldiarylmethane derivatives containing the 1-, 2-, 3-, and 9-phenanthryl groups have been synthesized from phenanthrene, and their properties investigated.